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Large, weakly-basic, bis(carboranyl)phosphines: An experimental and computational study †§

Laura E. Riley,^a Tobias Krämer,^{a*} Claire. L. McMullin,^b David Ellis,^a Georgina M. Rosair,^a Igor B. Sivaev^c and Alan J. Welch^{a*}

Abstract

The bis(carboranyl)phosphines [μ -2,2'-PPh-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**I**) and [μ -2,2'-PEt-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**1**) have been prepared and spectroscopically and structurally characterised. Crystallographic and DFT computational studies of **1** suggests that the orientation of the ethyl group, relative to the bis(carborane), is the result of intramolecular dihydrogen bonding. This orientation is such that the magnitudes of the $^2J_{\text{PH}}$ coupling constants are approximately equal but of opposite sign, and fast exchange between the methylene protons in solution leads to an observed $^2J_{\text{PH}}$ close to zero. The steric properties of **I**, **1** and their derivatives [μ -2,2'-P(Ph)AuCl-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**2**) and [μ -2,2'-P(Et)AuCl-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**3**) have been assessed by Tolman cone angle and percent buried volume calculations, from which it is concluded that the bis(carboranyl)phosphines **I** and **1** are comparable to PCy₃ in their steric demands. The selenides [μ -2,2'-P(Ph)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**4**) and [μ -2,2'-P(Et)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**5**) have also been prepared and characterised. The $^1J_{\text{PSe}}$ coupling constants for **4** and **5** are the largest yet reported for carboranylphosphine selenides and indicate that **I** and **1** are very weakly-basic.

^a Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, UK EH14 4AS. E-mail: t.kraemer@hw.ac.uk; a.j.welch@hw.ac.uk; Tel.: +44 (0)131 451 3259 (TK); +44 (0)131 451 3217 (AJW)

^b Department of Chemistry, University of Bath, Bath, UK BA2 7AY.

^c A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia

† Dedicated to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday.

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Introduction

One of the most currently active areas of carborane chemistry concerns the compound [1-(1'-1',2'-*closo*-C₂B₁₀H₁₁)-1,2-*closo*-C₂B₁₀H₁₁], two *ortho*-carborane units connected by a C–C bond¹ and commonly referred to as 1,1'-bis(*o*-carborane) (Fig. 1). Although it was first reported >50 years ago,² the chemistry of 1,1'-bis(*o*-carborane) was not fully explored for long periods because of the lack of a reliable, high-yielding synthesis. However, this has now been achieved³ and consequently a significant amount of new chemistry of 1,1'-bis(*o*-carborane) has recently appeared.⁴⁻²⁰

<Fig. 1 near here>

Several authors have taken advantage of the functionality of its C_{cage}H units to use 1,1'-bis(*o*-carborane) as a κ^2 ligand, binding transition-metals to the cage through two M–C σ -bonds, with recent studies^{7,8,13,19} building on the pioneering work of Hawthorne and co-workers.²¹ In marked contrast, very little has been reported concerning main group elements bound to 1,1'-bis(*o*-carborane). Zakharkin reported [μ -2,2'-AsMe-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] and [μ -2,2'-PPh-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**I**), although the latter was only poorly characterised,²²⁻²³ and Johnson and Knobler have described [μ -2,2'-PX-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}], X = Cl and F.²⁴ Very recently Peryshkov and co-workers isolated an interesting 12-vertex *closo*/12-vertex *nido* species with both bridging P(*i*-Pr)₂ and non-bridging PH(*i*-Pr)₂ units when attempting to add two P(*i*-Pr)₂ groups onto 1,1'-bis(*o*-carborane), one on each cage.¹⁷

In this contribution we expand on Zakharkin's early work, resynthesising **I** (in higher yield) and preparing the related μ -2,2'-PEt compound (**1**), with full characterisation of both bis(carboranyl)phosphines. All phosphines have potential in homogeneous catalysis, and consequently we have explored the steric and electronic properties of **I** and **1** *via* the synthesis and study of derivatives in which the P lone pair is bound to {–AuCl} and {=Se} fragments.

Results and Discussion

Bis(carboranyl)phosphines

Double deprotonation of 1,1'-bis(*o*-carborane) in Et₂O with *n*-BuLi in hexanes followed by treatment with PPhCl₂ affords [μ -2,2'-PPh-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**I**) as a white solid in 72% isolated yield, following work-up involving flash chromatography on silica. Although this bis(carboranyl)phosphine has been reported before it was previously characterised only by elemental analysis.²² We have studied the compound by mass spectrometry, multinuclear NMR spectroscopy and single-crystal X-ray diffraction.

The mass spectrum of **I** is dominated by a typical carborane envelope centred on m/z 392 corresponding to the molecular ion. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum contains resonances from δ *ca.* 0 to -13 ppm but is relatively uninformative in terms of detailed structure because of overlap of the lower-frequency resonances. The ^1H NMR spectrum confirms no $\text{C}_{\text{cage}}\text{H}$ resonances present and reveals the expected multiplets for ortho, meta and para H atoms which collapse to a doublet, apparent triplet and triplet, respectively, on ^{31}P decoupling. In the $^{31}\text{P}\{^1\text{H}\}$ spectrum is a simple singlet, δ 40.35 ppm.

The molecular structure of **I** is shown in Fig. 2. As anticipated the {PPh} fragment binds symmetrically to the bis(carborane) (the P1–C2 and P1–C2' distances are identical within experimental error), and only a small rotation of the Ph substituent about the P1–C11 bond would afford the molecule C_s symmetry, the likely time-averaged symmetry in solution. The formation of the PC2C1C1'C2' ring results in a slight bending of the spine of the bis(carborane) with angles B12...C1–C1' 169.14(16)° and B12'...C1'–C1 170.17(15)°, *c.f.* 175.14(5)° in 1,1'-bis(*o*-carborane) itself.¹

<Fig. 2 near here>

An analogous compound, [μ -2,2'-PEt-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**1**), was similarly prepared. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1** reveals a 2:2:6:2:2:6 pattern (high frequency to low frequency) between δ *ca.* 0 and -11 ppm, consistent with time-averaged C_s molecular symmetry. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum affords the expected quartet and triplet for the PCH₂CH₃ and PCH₂CH₃ resonances, respectively, and a singlet at δ 42.75 ppm is observed in the $^{31}\text{P}\{^1\text{H}\}$ spectrum.

There are two crystallographically-independent molecules of compound **1** in the asymmetric fraction of the unit cell, and Fig. 3 shows a perspective view of one of them, **1AB** (the other is **1CD**). Using the *Structure Overlay* tool in Mercury²⁵ the overall root-mean-square (rms) misfit between the {P(C₂B₁₀)₂} fragments of the two independent molecules (25 atoms) is 0.024 Å, with the greatest individual misfit between B4B and B4D, 0.049 Å. Including the C atoms of the Et groups results in only a marginal increase in the rms misfit to 0.029 Å (greatest individual misfit 0.073 Å between C12A and C12C) since the orientation of the ethyl group relative to the bis(carborane) in the two independent molecules is effectively the same.

<Fig. 3 near here>

This ethyl orientation is significant because of its influence on the ^1H NMR spectroscopic properties of **1** (*vide infra*). We believe the origin of the orientation is that it maximises intramolecular dihydrogen bonding between the weakly protonic CH atoms and the weakly hydridic BH atoms of the carborane cage, with the key CH...HB contacts shown in Fig. 4, an alternative view of **1AB**.

<Fig. 4 near here>

To investigate this further we have undertaken DFT calculations on compound **1**. The optimised (BP86-D3/def2-TZVP/def2-SVP) geometry, **1_{DFT}** (Fig. 5), is in excellent agreement with the structure determined crystallographically (see ESI for key optimised bond parameters), including the orientation of the ethyl group. Thus the overall rms misfit between computed and experimental {P(C₂B₁₀)₂} fragments (using molecule **1AB**) is only 0.019 Å (greatest individual misfit 0.031 Å for P1), rising to only 0.029 Å if the ethyl C atoms are included (greatest individual misfit 0.081 Å for C12A). In terms of the ethyl group orientation the experimental lp–P–C11–C12 torsion angles are 38.8(4)° and 42.5(4)° for **1AB** and **1CD**, respectively, and the computed torsion angle is 38.4°. Moreover, the DFT study provides strong support for the presence of dihydrogen bonding. A topological analysis of the electron density in **1_{DFT}** using the QTAIM methodology reveals bond critical points (BCP) between H11PX and the cage hydrogen atoms H3 and H6', located roughly at the centre of each bond vector (see Figure S1 for a molecular graph). Additional albeit somewhat weaker interactions are present for H11QY/H7 and H12R/H11 (see Fig. S1). Both the electron density $\rho(r)$ (0.007-0.011 a.u.) and its Laplacian $\nabla^2\rho(r)$ (0.022-0.038 a.u.) at the relevant BCPs are diagnostic of typical closed-shell interactions and fall within the ranges proposed for dihydrogen bonds.²⁶

<Fig. 5 near here>

An interesting feature of the ¹H NMR spectrum of compound **1** is the lack of observable coupling between the PCH₂CH₃ H atoms and the P atom. Thus, whilst the PCH₂CH₃ H atoms appear as a doublet (³J_{PH} = 23.0 Hz) of triplets (³J_{HH} = 7.9 Hz) the PCH₂CH₃ H atoms appear as only a simple quartet (³J_{HH} = 7.9 Hz). A ¹H-³¹P HMBC experiment shows the presence of the expected coupling between the P atom and the PCH₂CH₃ H atoms but, additionally, a weak correlation between signals due to P and CH₂CH₃. The lack of any observable splitting in the 1D ¹H spectrum suggests that the value of ²J (¹H-³¹P) is of the order of the ¹H resonance linewidth (estimated to be *ca.* 1 Hz).

An understanding of the origin of this small 2-bond P-H coupling comes from the DFT calculations on compound **1**. The computed energy profile for ethyl rotation about the P–C11 vector (Fig. 6) establishes that **1_{DFT}** and its isoenergetic rotational conformer **1'_{DFT}** dominate the equilibrium distribution, whilst the Boltzmann population of the symmetrical isomer **1''_{DFT}** (+4 kcal·mol⁻¹) is near zero at room temperature. Importantly, due to the low energetic barrier associated with **TS(1_{DFT}-1'_{DFT})** separating **1_{DFT}** and **1'_{DFT}** ($\Delta G^\ddagger = +1.8$ kcal·mol⁻¹) the methylene protons can undergo rapid exchange in solution. Calculated averaged ³J_{PH} (calc. 26.2 Hz; exp.: 23.0 Hz) and ³J_{HH} (calc.: 9.7 Hz; exp.: 7.9 Hz) coupling constants are in good agreement with the experimental values. The values of ²J_{PH} for coupling to the individual

methylene hydrogen atoms are of the same order of magnitude but, importantly, they are of opposite sign (for H11PX $^2J_{\text{PH}} = -5.4$ Hz whilst for H11QY $^2J_{\text{PH}} = +5.6$ Hz). Hence, fast exchange between these hydrogen atoms reduces the observed $^2J_{\text{PH}}$ to approximately zero, in line with the experimental upper limit of $\sim \pm 1$ Hz. The predominant contribution to the total coupling constant is associated with the Fermi contact term.

<Fig. 6 near here>

With the characterisations of **I** and **1** now complete, we turn to their derivatives. Phosphines are ligands of great importance in homogeneous catalysis by transition-metal complexes,²⁷ and carboranylphosphines have been used extensively in a variety of catalytic applications.²⁸ The two key characteristics of phosphines as ligands in catalysis are their size and basicity, and we have targeted and studied derivatives of **I** and **1** specifically to assess these features.

Steric Properties

The steric demand of a phosphine is classically assessed by its Tolman cone angle (θ),²⁹ and we have used the crystallographically-determined structures of **I** and **1** to measure these. In addition, a recent alternative to θ is Cavallo and Nolan's percent buried volume parameter, $\%V_{\text{bur}}$.³⁰ Although originally developed for NHCs, $\%V_{\text{bur}}$ has been shown to scale linearly with θ for a range of phosphines and, furthermore, there is a strong linear relationship between θ of PR_3 and $\%V_{\text{bur}}$ of the adduct R_3PAuCl .³¹ For this reason we have prepared and studied the gold-chloride adducts of compounds **I** and **1**.

Treatment of a solution of **I** or **1** in DCM with an equimolar amount of (tht)AuCl affords the new species $[\mu\text{-}2,2'\text{-P(Ph)AuCl}\{1\text{-(1'-1',2'-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})\text{-}1,2\text{-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10}\}]\text{ (2)}$ and $[\mu\text{-}2,2'\text{-P(Et)AuCl}\{1\text{-(1'-1',2'-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})\text{-}1,2\text{-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10}\}]\text{ (3)}$ as white solids in 81 and 32% yields, respectively.

Compounds **2** and **3** were initially characterised by mass spectrometry and ^1H , ^{11}B and ^{31}P NMR spectroscopies. The $^{11}\text{B}\{^1\text{H}\}$ spectrum of **2** is largely uninformative because of multiple overlapping resonances, but that of **3** is sufficiently well-resolved to allow integration which is consistent with time-averaged C_s molecular symmetry in solution at room temperature. In both **2** and **3** the $^{31}\text{P}\{^1\text{H}\}$ spectrum reveals a simple singlet, shifted *ca.* 28 and 33 ppm, respectively, to high frequency relative to those in **I** and **1**. The ^1H NMR spectrum of **2** shows the anticipated multiplets for the phenyl protons, whilst for **3** the H atoms of the ethyl group appear as a doublet of quartets (PCH_2CH_3) and a doublet of triplets (PCH_2CH_3).

The molecular structures of **2** and **3**, as determined crystallographically, are shown in Figs. 7 and 8, respectively. In both cases co-ordination to the $\{\text{AuCl}\}$ fragments causes minimal change in the structures of the bis(carboranyl)phosphines, with the same orientations of the Ph

groups or Et groups being effectively maintained between **I** and **2** and between **1** and **3**. Moreover, a DFT-optimised study of **3** was fully consistent with its crystallographic counterpart; a structure overlay of **3** and **3_{DFT}** yielded an overall rms misfit of 0.018 Å for {P(C₂B₁₀)₂} fragments (greatest individual misfit 0.027 Å for B5') rising to only 0.020 Å if the ethyl carbon atoms were included (greatest misfit 0.033 Å for C11). The overlay is somewhat poorer if the {AuCl} fragment is included, with the overall misfit increasing to 0.077 Å and the Cl atoms misfitting by 0.345 Å.

<Fig. 7 near here>

<Fig. 8 near here>

The Tolman cone angle for **I** is calculated to be 172.5°, whilst that for **1** is 171.6° (Table 1). Although Ph is a larger substituent than Et, the similarity of the cone angles for **I** and **1** reflects the fact that the vast majority of the steric bulk of **I** and **1** comes from the common bis(carborane) fragment. Percent buried volumes for **I** and **1** are calculated to be 32.0 and 30.8 (average), respectively. Co-ordination to {AuCl} to afford **2** and **3**, respectively, results in small increases in both θ and % V_{bur} . This arises because the stereochemical influence of the P lone pair of electrons on the bis(carborane) and Ph/Et substituents is reduced on co-ordination, allowing small increases in the C–P–C angles and producing a slightly bulkier ligand.

<Table 1 near here>

Comparing the θ and % V_{bur} values for **I**, **1**, **2** and **3** with analogous species in the literature we conclude that the bis(carboranyl)phosphines **I** and **1** are, in terms of their size, most comparable to (but slightly larger than) tricyclohexylphosphine, PCy₃.³¹

Electronic Properties

The basicity of phosphines PR₃ is conveniently assessed by measurement of the 1-bond P–Se coupling constant, ¹J_{PSe}, of the corresponding selenide R₃P=Se; the more electron-withdrawing the substituents (*i.e.* the less basic the phosphine) the greater the degree of 3s character in the phosphorus lone pair and the greater the magnitude of ¹J_{PSe}.³² Accordingly we have synthesised [μ-2,2'-P(Ph)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**4**) and [μ-2,2'-P(Et)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**5**), the selenides of **I** and **1** respectively, by the simple process of heating the bis(carboranyl)phosphine with an excess of elemental Se in toluene. Scheme 1 summarises all the syntheses reported in this paper.

<Scheme 1 near here>

Compounds **4** and **5** are afforded as pale-pink solids in reasonable isolated yields. Both show the anticipated molecular ion peaks in their mass spectra. Their ¹¹B{¹H} NMR spectra

are relatively uninformative due to considerable overlap of resonances. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are singlets at δ *ca.* 50 and 58 ppm, respectively, at higher frequency than in the corresponding bis(carboranyl)phosphine but not as deshielded as in the AuCl compounds **2** and **3**. The ^1H NMR spectra of **4** and **5** show the expected resonances for the Ph or Et substituents, including a doublet of quartets for the PCH_2CH_3 resonance of **5** with $^2J_{\text{PH}} = 11.6$ Hz, and the re-emergence of this 2-bond P-H coupling can be understood in terms of the rehybridisation of the phosphorus orbitals induced by coordination of the P lone pair to the $\{\text{=Se}\}$ fragment.³³ These changes closely follow the general trends observed for P(III) and P(V) compounds.³⁴ The computed averaged geminal $^2J_{\text{PH}}$ coupling constant in **5**_{DFT} increases to -14.1 Hz, a value in good agreement with experiment ($^2J_{\text{PH}} = 11.6$ Hz). We note that the phase information of the coupling constant is invisible in first-order NMR-spectra, and thus all coupling constants appear to be positive. The observed decrease of $^2J_{\text{PH}}$ (or increase of the modulus $|^2J_{\text{PH}}|$) can be correlated with the admixture of a higher degree of $3s$ character into the P bonds, rendering the hybridisation around P close to sp^3 , as borne out in the NBO analysis of the associated P–C bonding orbitals (21–26% s , 73–78% p). This is paralleled by a notable reduction of P $3s$ character in the P–Se σ -bond (32% s , 67% p), compared to 52% $3s$ character of the phosphorous lone pair in **1**_{DFT}. This change of the electron distribution around P as the lone pair is replaced by Se in **5**_{DFT} in turn reinforces the direct Fermi contact contribution to the 1- and 2-bond coupling pathways (see ESI for more detail).

Of relevance to the basicities of the bis(carboranyl)phosphine parent compounds **I** and **1**, the $^{31}\text{P}\{^1\text{H}\}$ spectra of **4** and **5** show clear Se satellites with $^1J_{\text{PSe}} = 891$ and 894 Hz, respectively.³⁵ These coupling constants are considerably larger than those of a range of common phosphines [typically 670–750 Hz, Table 1 of ref. 32(d)] suggesting that **I** and **1** are very weakly-basic. There are few carboranylphosphine selenides in the literature, but those that are known all have relatively large values of $^1J_{\text{PSe}}$. In $[\text{1-P(Se)Ph}_2\text{-2-PPh}_2\text{-1,2-}i\text{-closo-C}_2\text{B}_{10}\text{H}_{10}]$ $^1J_{\text{PSe}} = 807$ Hz, whilst in the 2-Me and 2-Ph analogues $^1J_{\text{PSe}} = 804$ and 812 Hz, respectively.³⁶ Clearly, these large couplings are the result of the strong electron-withdrawing property of carboranes relative to alkyl or aryl substituents, and we attribute the even larger $^1J_{\text{PSe}}$ values in **4** and **5** to the fact that here the $\{\text{P=Se}\}$ fragment is directly bonded to two carborane cages. Consistent with this, Viñas and co-workers have described species $[\mu\text{-1,1'-P(R)Se-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_{10})_2]^-$ in which the $\{\text{P(R)Se}\}$ fragment is also attached to two heteroborane cages and report $^1J_{\text{PSe}}$ values of 833 Hz ($\text{R} = \text{Ph}$) and 679 Hz ($\text{R} = t\text{-Bu}$).³⁷ In the related species $[\text{8,8'-}\mu\text{-(1'',2''-C}_6\text{H}_4\text{)-}\mu\text{-1,1'-P(R)Se-3,3'-Co(1,2-C}_2\text{B}_9\text{H}_9)_2]^-$ $^1J_{\text{PSe}}$ is 848 Hz ($\text{R} = \text{Ph}$) and 692 Hz ($\text{R} = t\text{-Bu}$), respectively.³⁷

Overall, the magnitudes of $^1J_{\text{PSe}}$ recorded for **4** and **5** are currently the largest reported for carboranylphosphine selenides, implying that the parent phosphines **I** and **1** are very weakly-

basic. Note that, in principle, the degree of *s* character in the phosphorus lone pair in PR₃ can be influenced not only by the electron-withdrawing properties but also the size of the substituents. In this respect we recall that **I** and **1** are comparable in their steric demands to PCy₃. They are, however, much less basic, since ¹J_{PSe} in Cy₃P=Se is only 673 Hz.³⁸

Compounds **4** and **5** were also studied crystallographically, and perspective views of single molecules are shown in Figs. 9 and 10, respectively. As noted above, compound **5** was also studied computationally, again affording excellent agreement with the crystallographic structure; for the {P(C₂B₁₀)₂} fragments of **5** and **5_{DFT}** the rms misfit is 0.020 Å (worst individual misfit 0.034 Å for B11'), rising to only 0.034 Å (poorest individual fit 0.100 Å for C11) when the ethyl C atoms are included and 0.036 Å (worst fit 0.098 Å, C12) when the Se atom is added. Once again, the general orientation of the Ph or Et substituent relative to the bis(carborane) moiety is maintained, with torsion angles lp/Au/Se–P–C11–C12 broadly consistent for **I**, **2** and **4** (Ph substituents) and for **1**, **1_{DFT}**, **3**, **3_{DFT}**, **5** and **5_{DFT}** (Et substituents) albeit with a *ca.* 10° increase for the selenides **4** and **5** (Table 2). As previously noted, for the ethyl species **1**, **3** and **5** this orientation is traced to intramolecular dihydrogen bonding involving H11A (H11P and H11X in **1**) with H6' and with H3, whilst for the phenyl compounds **I**, **2** and **4** H16 of the phenyl ring is seen to interact primarily with H6' and to a lesser extent with H3.

<Fig. 9 near here>

<Fig. 10 near here>

<Table 2 near here>

The P=Se distances in **4** and **5** are 2.0798(6) and 2.0801(7) Å, respectively. These are significantly shorter than that in Cy₃P=Se, 2.108(1) Å,³⁹ and those in recent compilations of P=Se distances.^{38,40} In fact the P=Se distances in **4** and **5** are amongst the shortest yet reported; of 378 structures containing the fragment {R¹R²R³P=Se} in the Cambridge Structural Database⁴¹ only seven have P=Se distances <2.08 Å.⁴² Short P=Se distances in **4** and **5** are fully consistent with a significant degree of *s* character in the phosphorus lone pair of **I** and **1**, as implied from the ¹J_{PSe} values.

Conclusions

The bis(carboranyl)phosphines **I** and **1** are comparable in their steric demands to PCy₃ but are much less basic. In fact, in terms of their ¹J_{PSe} values, **I** and **1** are the least basic of any carboranylphosphines so far reported. As large, weakly-basic phosphines **I** and **1** have potential as ligands in homogeneous catalysis, and future contributions will develop this theme.

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Experimental

Synthesis

Experiments were performed under dry, oxygen free N₂, using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. Solvents were either freshly distilled under nitrogen from the appropriate drying agent [THF, Et₂O and 40-60 petroleum ether (petrol); sodium wire: CH₂Cl₂ (DCM); calcium hydride] or were purified by an MBRAUN SPS-800 and stored over 4 Å molecular sieves, and all were degassed (3×freeze-pump-thaw cycles) before use. Preparative TLC employed 20×20 cm Kieselgel F₂₅₄ glass plates and for column chromatography we used 60 Å silica as the stationary phase. NMR spectra at 400.1 MHz (¹H), 128.4 MHz (¹B) or 162.0 MHz (³¹P) were recorded on a Bruker DPX-400 spectrometer from CDCl₃ solutions at 298 K, using CDCl₃ stored over 4 Å molecular sieves. Electron impact mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer (University of Edinburgh). The starting materials 1,1'-bis(*o*-carborane) ³ and (tht)AuCl ⁴³ were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

[μ-2,2'-PPh-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (I). *n*-BuLi (2.79 mL of 2.5 M solution in hexanes, 6.975 mmol) was added dropwise to a cooled (0 °C) solution of 1,1'-bis(*o*-carborane) (1.000 g, 3.491 mmol) in Et₂O (20 mL) and the products were stirred for 1 h at room temperature. The pale yellow solution was cooled to 0 °C then PPhCl₂ (0.47 mL, 3.491 mmol) in Et₂O (10 mL) was added over 30 mins to give a green-yellow solution which was subsequently heated to reflux for 2 h producing a pale yellow solution. Once cooled this was filtered and the solvent removed *in vacuo*. Purification by flash chromatography (petrol) yielded a white solid subsequently identified as [μ-2,2'-PPh-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (I) (0.981 g, 2.499 mmol, 72%). ¹¹B{¹H} NMR, δ -0.1 (2B), -3.9 to -11.2 [overlapping resonances with maxima at -3.9, -6.4, -8.7, -9.8, -11.2 (18B)]. ¹H NMR, δ 7.77-7.73 (m, 2H, C₆H₅), 7.65-7.62 (m, 1H, C₆H₅), 7.59-7.54 (m, 2H, C₆H₅). ¹H{³¹P} NMR, δ 7.76 (d, ³J_{HH} = 7.1 Hz, 2H, C₆H₅), 7.64 (t, ³J_{HH} = 7.4 Hz, 1H, C₆H₅), 7.57 (app t, ³J_{HH} = 7.1 Hz, 2H, C₆H₅). ³¹P{¹H} NMR, δ 40.35 (s). EIMS, envelope centred on *m/z* 392.3 (M⁺).

[μ -2,2'-PEt-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (1). *n*-BuLi (0.56 mL of a 2.5 M solution in hexanes, 1.396 mmol) was added dropwise to a cooled (0 °C) solution of 1,1'-bis(*o*-carborane) (0.200 g, 0.698 mmol) in THF (10 mL) and the products stirred for 1 h. The pale yellow solution was frozen at -196 °C then PEtCl₂ (0.70 mL of a 1.0 M solution in THF, 0.698 mmol) was added and the reaction mixture stirred overnight at room temperature giving a colourless solution. Volatiles were removed *in vacuo* and the crude mixture dissolved in DCM and filtered. Purification by flash chromatography (petrol) followed by preparative TLC (DCM:petrol, 1:19) yielded a white solid (*R*_f = 0.97) subsequently identified as [μ -2,2'-PEt-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (1) (0.154 g, 0.447 mmol, 64%). ¹¹B{¹H} NMR, δ -0.3 (2B), -3.8 (2B), -6.6 (6B), -7.6 (2B), -8.5 (2B), -10.6 (6B). ¹H NMR, δ 1.98 (q, 2H, PCH₂CH₃, ³*J*_{HH} = 7.9 Hz), 1.31 (dt, 3H, PCH₂CH₃, ³*J*_{HH} = 7.9 Hz, ³*J*_{PH} = 23.0 Hz). ¹H{³¹P} NMR, δ 1.99 (q, 2H, PCH₂CH₃, ³*J*_{HH} = 7.9 Hz), 1.32 (t, 3H, PCH₂CH₃, ³*J*_{HH} = 7.9 Hz). ³¹P{¹H} NMR, δ 42.75 (s). EIMS, envelope centred on *m/z* 344.3 (M⁺).

[μ -2,2'-P(Ph)AuCl-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (2). A DCM (5 mL) solution of **I** (0.100 g, 0.255 mmol) was transferred *via* cannula to a DCM (10 mL) solution of (tht)AuCl (0.082 g, 0.256 mmol) at 0 °C. The colourless solution was stirred at 0 °C for 30 min, then reduced to *ca.* 3 mL *in vacuo*. Petrol (10 mL) was added to afford a white precipitate which was collected by filtration and washed with petrol (10 mL) to give a white solid subsequently identified as [μ -2,2'-P(Ph)AuCl-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (2) (0.129 g, 0.206 mmol, 81%). ¹¹B{¹H} NMR, δ -1.87 (2B), -0.7 to -13.9 [overlapping resonances with maxima at -3.6, -5.6, -7.6, -9.2, -10.9 (18B)]. ¹H NMR, δ 8.15-8.09 (m, 2H, C₆H₅), 7.86-7.81 (m, 1H, C₆H₅), 7.75-7.70 (m, 2H, C₆H₅). ³¹P{¹H} NMR, δ 68.96 (s). EIMS, envelope centred on *m/z* 624.1 (M⁺).

[μ -2,2'-P(Et)AuCl-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (3). Similarly, from compound **1** (0.100 g, 0.290 mmol) and (tht)AuCl (0.093 g, 0.290 mmol) was isolated [μ -2,2'-P(Et)AuCl-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (3) (0.053 g, 0.092 mmol, 32%) as a white solid. ¹¹B{¹H} NMR, δ 1.7 (2B), -3.3 (2B), -5.7 (6B), -7.6 (4B), -10.4 (6B). ¹H NMR, δ 2.48 (dq, 2H, PCH₂CH₃, ²*J*_{PH} = 10.9 Hz, ³*J*_{HH} = 7.7 Hz), 1.52 (dt, 3H, PCH₂CH₃, ³*J*_{PH} = 27.9 Hz, ³*J*_{HH} = 7.7 Hz). ³¹P{¹H} NMR, δ 75.76 (s). EIMS, envelope centred on *m/z* 577.3 (M⁺).

[μ -2,2'-P(Ph)Se-{1-(1'-1',2'-closo-C₂B₁₀H₁₀)-1,2-closo-C₂B₁₀H₁₀}] (4). Elemental selenium (0.201 g, 2.546 mmol) was added to a toluene (10 mL) solution of **I** (0.100 g, 0.225 mmol) which was then heated to reflux for 72 h. Excess selenium was removed by filtration and ³¹P{¹H} NMR spectroscopy revealed a 74% conversion of **I** to a new species. Preparative TLC (DCM:petrol, 1:9) yielded a colourless band at *R*_f = 0.59 from which the product, [μ -

2,2'-P(Ph)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**4**), was isolated as a pale-pink solid (0.057 g, 0.120 mmol, 47%). ¹¹B{¹H} NMR, δ 1.2 (2B), -4.1 to -11.2 [overlapping resonances with maxima at -4.1, -6.0, -6.4, -8.5, -9.9, -11.2 (18B)]. ¹H NMR, δ 8.31-8.25 (m, 2H, C₆H₅), 7.73-7.68 (m, 1H, C₆H₅), 7.63-7.57 (m, 2H, C₆H₅). ³¹P{¹H} NMR, δ 50.52 (s + Se satellites, ¹J_{PSe} = 891 Hz). EIMS, envelope centred on *m/z* 471.3 (M⁺).

[μ-2,2'-P(Et)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**5**). Similarly, from Se (0.241 g, 3.052 mmol) and compound **1** (0.100 g, 0.145 mmol) was prepared [μ-2,2'-P(Et)Se-{1-(1'-1',2'-*closo*-C₂B₁₀H₁₀)-1,2-*closo*-C₂B₁₀H₁₀}] (**5**), a pale-pink solid (71% conversion by ³¹P{¹H} NMR, isolated yield 0.049 g, 0.116 mmol, 38%). ¹¹B{¹H} NMR, δ 0.9 (2B), -3.7 (2B), -6.2 to -10.6 [overlapping resonances with maxima at -6.2, -7.6, -8.7, -9.2, -10.6 (16B)]. ¹H NMR, δ 2.72 (dq, 2H, PCH₂CH₃, ²J_{PH} = 11.6 Hz, ³J_{HH} = 7.6 Hz), 1.52 (dt, 3H, PCH₂CH₃, ³J_{PH} = 25.9 Hz, ³J_{HH} = 7.6 Hz). ³¹P{¹H} NMR, δ 58.05 (s + Se satellites, ¹J_{PSe} = 894 Hz). EIMS, envelope centred on *m/z* 423.4 (M⁺).

Crystallography

Diffraction-quality crystals of all compounds were obtained by slow evaporation of a solution of the appropriate compound: **1**, **1** and **4**; petrol: **2** and **3**; DCM: **5**; CDCl₃. Intensity data were collected on a Bruker X8 APEXII diffractometer using Mo-K_α X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.⁴⁴ Using OLEX2⁴⁵ structures were solved by Direct Methods using the SHELXS⁴⁶ or SHELXT⁴⁷ programme and refined by full-matrix least-squares (SHELXL).⁴⁶

All crystals were single except those of **5** which was treated as a two-component twin. All crystals were also fully ordered and solvate-free, except those of compound **3**. In **3** the gold carboranylphosphine complex is fully ordered but there is disordered solvent in the lattice that was impossible to satisfactorily model. Hence for this structure the intensity contribution of the disordered solvent was removed using the BYPASS procedure⁴⁸ implemented in OLEX2. The total electron count of solvent per cell was 420 e which corresponds to 10 DCM molecules. These disordered solvent molecules predominantly occupy four voids of *ca.* 270 Å³ each.

For all structures H atoms bound to cage B atoms were allowed to refine positionally whilst H atoms bound to C atoms were constrained to idealised geometries; C_{phenyl}-H = 0.95 Å, C_{methyl}-H = 0.98 Å, C_{methylene}-H = 0.99 Å. All H displacement parameters, *U*_{iso}, were constrained to be 1.2×*U*_{eq} (bound B or C) except Me H atoms [*U*_{iso}(H) = 1.5×*U*_{eq} C(Me)]. Table 3 contains further experimental details.

<Table 3 near here>

Cone Angle and Percent Buried Volume Calculations

Bis(carborane)phosphine cone angles were calculated from the crystallographically-determined structures using both the free bis(carborane)phosphines (compounds **I** and **1**) and their AuCl complexes (compounds **2** and **3**), using the method of Müller and Mingos.⁴⁹ The P–M distance was set at 2.28 Å. % V_{bur} calculations were performed (again on all compounds **I**, **1-3**) using the SambVca software of Cavallo and co-workers,⁵⁰ with a sphere radius of 3.5 Å, a P–M distance of 2.28 Å and scaled Bondi radii.

Computational Methods

All electronic structure calculations were carried out using the Gaussian 09 (Revision D.01)⁵¹ program suite at the DFT level of theory. Geometries of all compounds were fully optimised without imposing symmetry constraints (C_1 symmetry), employing the BP86 functional.⁵² Ahlrich's def2-TZVP basis of triple- ζ quality was used on P, Au, Cl, Se, C and all hydrogen atoms of the ethyl group, while all B–H units of the carborane cage were described with the def2-SVP basis set.⁵³ The core electrons in Au were replaced by the Stuttgart-Dresden scalar relativistic effective core potential (SDD, ECP60MWB).⁵⁴ Optimised stationary points were characterised by analysis of their analytical second derivatives, with minima having only positive eigenvalues and transition states having exactly one imaginary eigenvalue. Subsequent geometry optimisations in both directions of the reaction coordinate were performed to confirm the minima linked by each transition state. The frequency calculations also provided thermal and entropic corrections to the total energy in gas phase at $T = 298.15$ K and $p = 1$ atm within the rigid-rotor/harmonic oscillator (RRHO) approximation. Dispersion effects were accounted for by applying Grimme's van der Waals correction (D3 parameterization) protocol including Becke-Johnson damping during the optimisations.⁵⁵ The topology of the electron density was analysed by means of QTAIM (quantum theory of atoms in molecules),⁵⁶ as implemented in the AIMAll package.⁵⁷ For **3-DFT**, inner shell electrons on Au modelled by the ECP were fitted by core density functions. Isotropic NMR spin-spin coupling constants were calculated using the coupled-perturbed SCF⁵⁸ method with the BHandHLYP⁵⁹ functional, which was found to yield the best agreement with experimental couplings. The J -couplings were obtained as the sum of all four Ramsey terms, *i.e.* Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbit (PSO), diamagnetic-spin orbit (DSO). The reported coupling constants have been averaged assuming free internal molecular rotation. The basis sets stated above were replaced by aug-cc-pVTZ-J⁶⁰ on P, and ethyl (C, H), as well as the cc-pVDZ⁶¹ basis set (and associated ECP for Au) on all other atoms. Effects due to the presence of a solvent were treated implicitly with a polarisable

dielectric model, using the IEFPCM formalism in conjunction with Truhlar's SMD model.⁶² The chosen dielectric constant ($\epsilon = 4.71$) corresponds to that of chloroform. Compositions of molecular orbitals were analysed within the framework of localised natural bond orbitals, using the NBO 6.0 software.⁶³

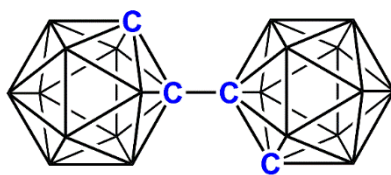


Fig. 1 1,1'-bis(*o*-carborane).

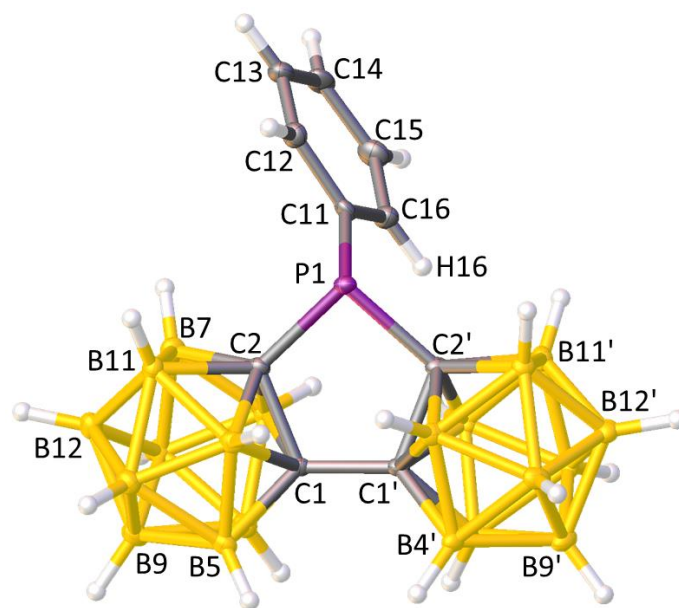


Fig. 2 Perspective view of **I** with atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level except for H atoms. Selected interatomic distances (Å): P1–C2 1.893(3), P1–C2' 1.887(3), P1–C11 1.819(3), C1–C1' 1.534(3).

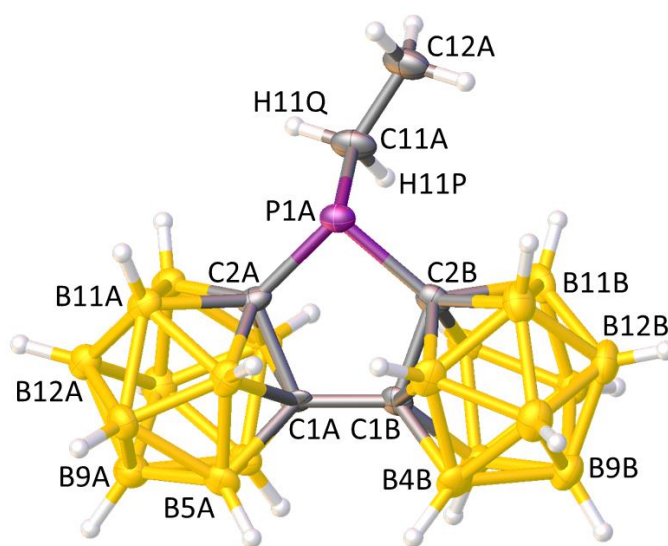


Fig. 3 Perspective view of one of the two crystallographically-independent molecules of compound **1** (**1AB**) with atomic numbering scheme. Molecule **1CD** is practically superimposable. Displacement ellipsoids as in Fig. 2. Selected interatomic distances (Å): P1A–C2A 1.870(5), P1A–C2B 1.890(5), P1A–C11A 1.844(5), C1A–C1B 1.533(7); P1C–C2C 1.886(5), P1C–C2D 1.890(5), P1C–C11C 1.818(5), C1C–C1D 1.530(6).

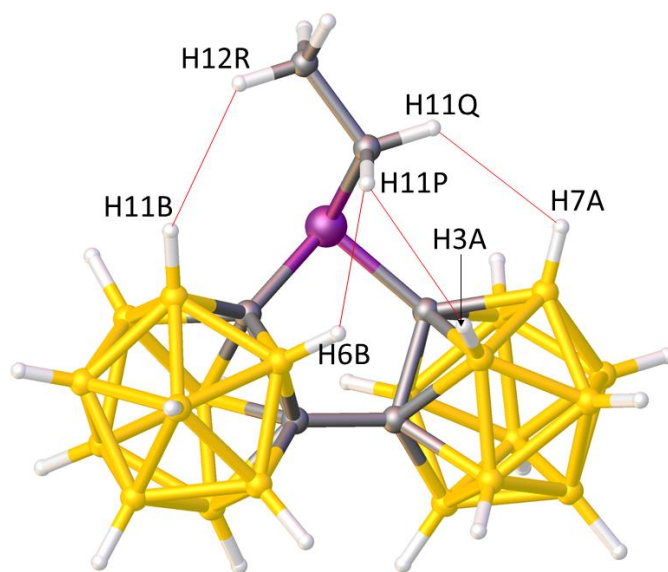


Fig. 4 Alternative view of **1AB** showing dihydrogen bonds as red lines. Interatomic distances (Å): H11P...H3A 2.45(4), 2.39(4), **2.28**; H11P...H6B 2.28(5), 2.29(5), **2.10**; H11Q...H7A 2.46(5), 2.47(4), **2.36**; H12R...H11B 2.51(5), 2.40(5), **2.31**. Values in *italics* are the equivalent distances in molecule **1CD**, and values in **bold** are those from the DFT study of **1**.

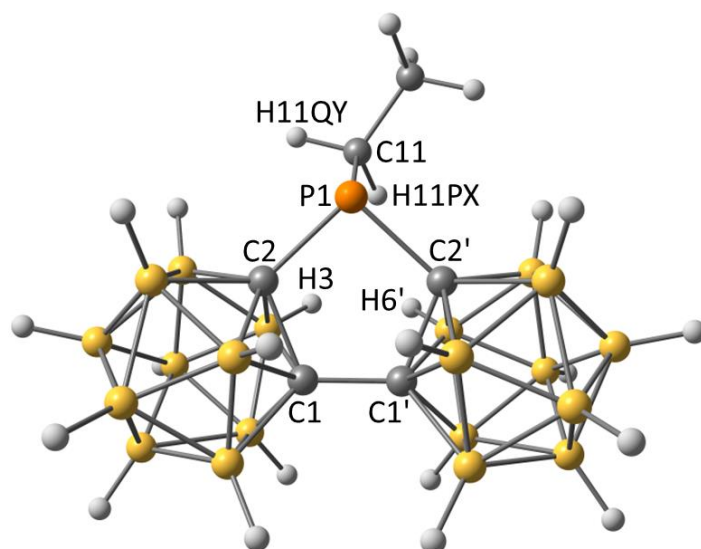


Fig. 5 DFT-optimised structure of **1**. Note the excellent agreement with the experimentally-determined structure (Fig. 3), including the orientation of the Et group. Selected interatomic distances (Å): P1–C2 1.889, P1–C2' 1.892, P1–C11 1.852, C1–C1' 1.528.

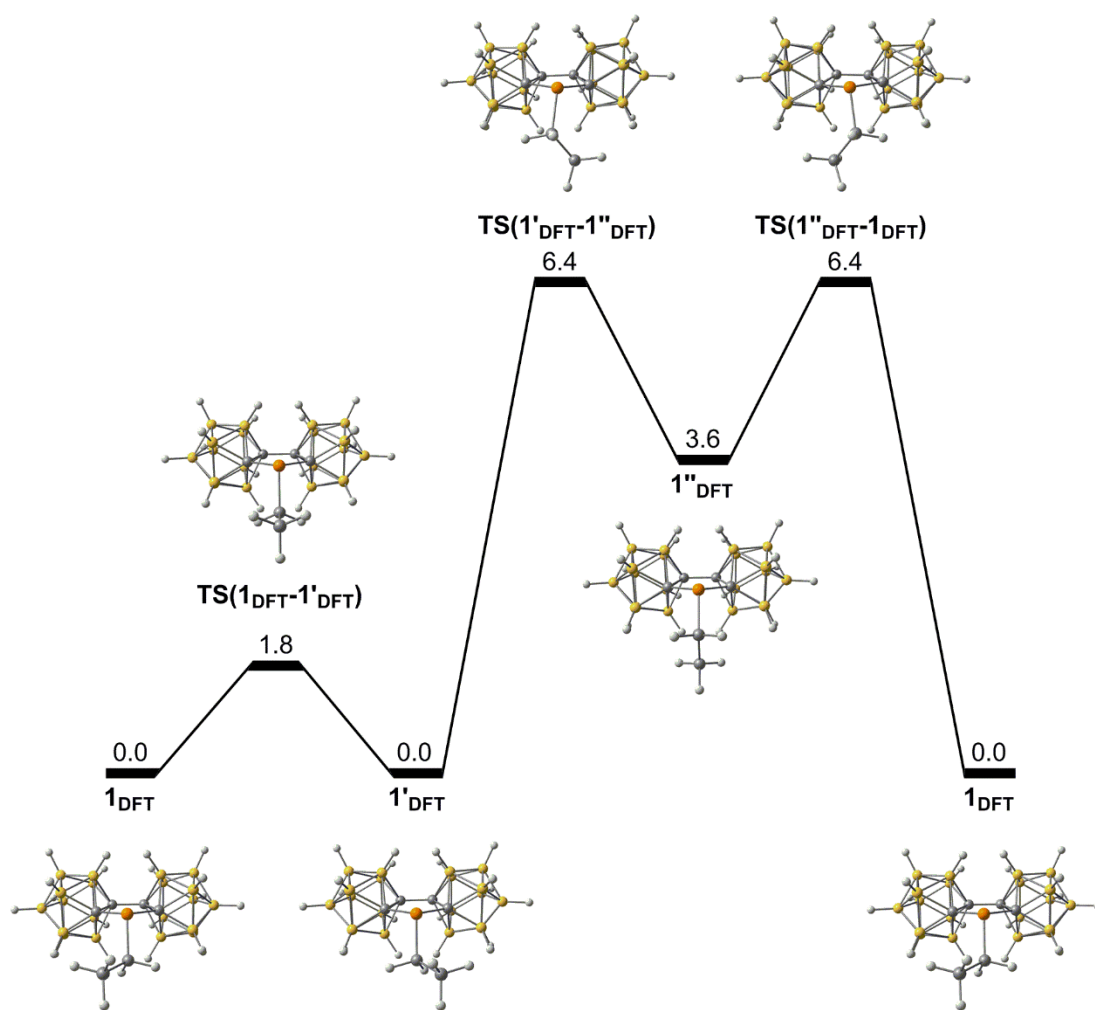


Fig. 6 Calculated Gibbs Free Energy profile (kcal·mol⁻¹) for ethyl rotation in **1_{DFT}** (BP86-D3/def2-TZVP/def2-SVP). Boltzmann populations: **1_{DFT}** 50% **1'_{DFT}** 50% **1''_{DFT}** 0%.

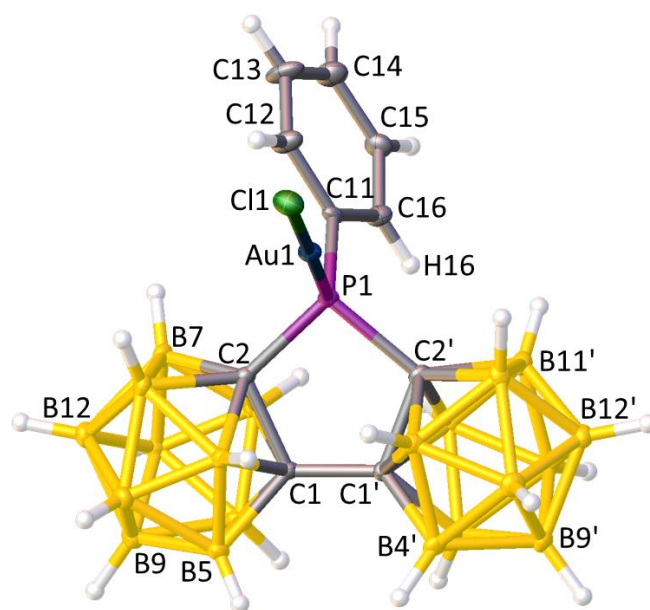


Fig. 7 Perspective view of compound **2** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2. Selected interatomic distances (Å): P1–Au1 2.2217(8), Au1–Cl1 2.2698(8), P1–C2 1.878(3), P1–C2' 1.879(3), P1–C11 1.797(3), C1–C1' 1.523(4).

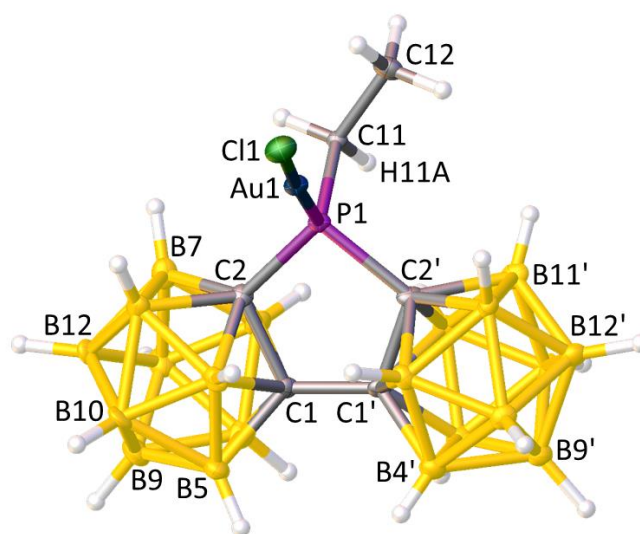


Fig. 8 Perspective view of compound **3** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2. Selected interatomic distances (Å): P1–Au1 2.2181(11), Au1–Cl1 2.2910(11), P1–C2 1.860(4), P1–C2' 1.883(4), P1–C11 1.816(4), C1–C1' 1.538(5).

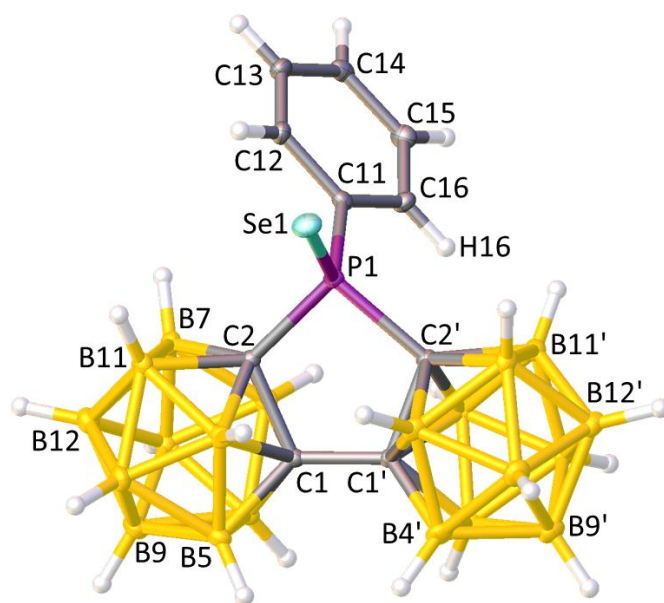


Fig. 9 Perspective view of compound **4** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2. Selected interatomic distances (Å): P1–Se1 2.0798(6), P1–C2 1.8860(19), P1–C2' 1.896(2), P1–C11 1.810(2), C1–C1' 1.536(3).

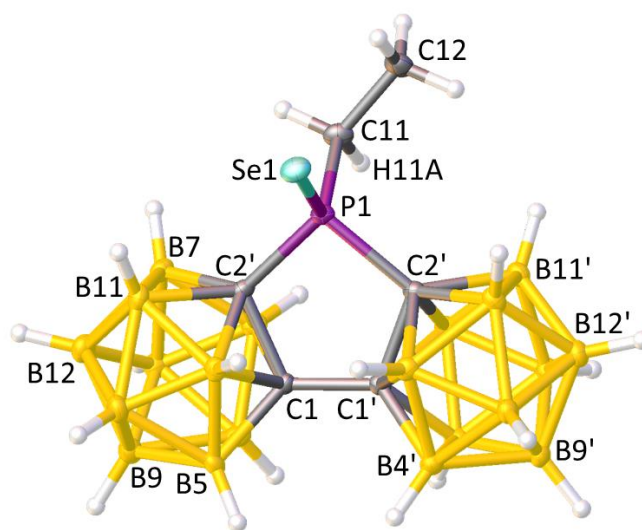
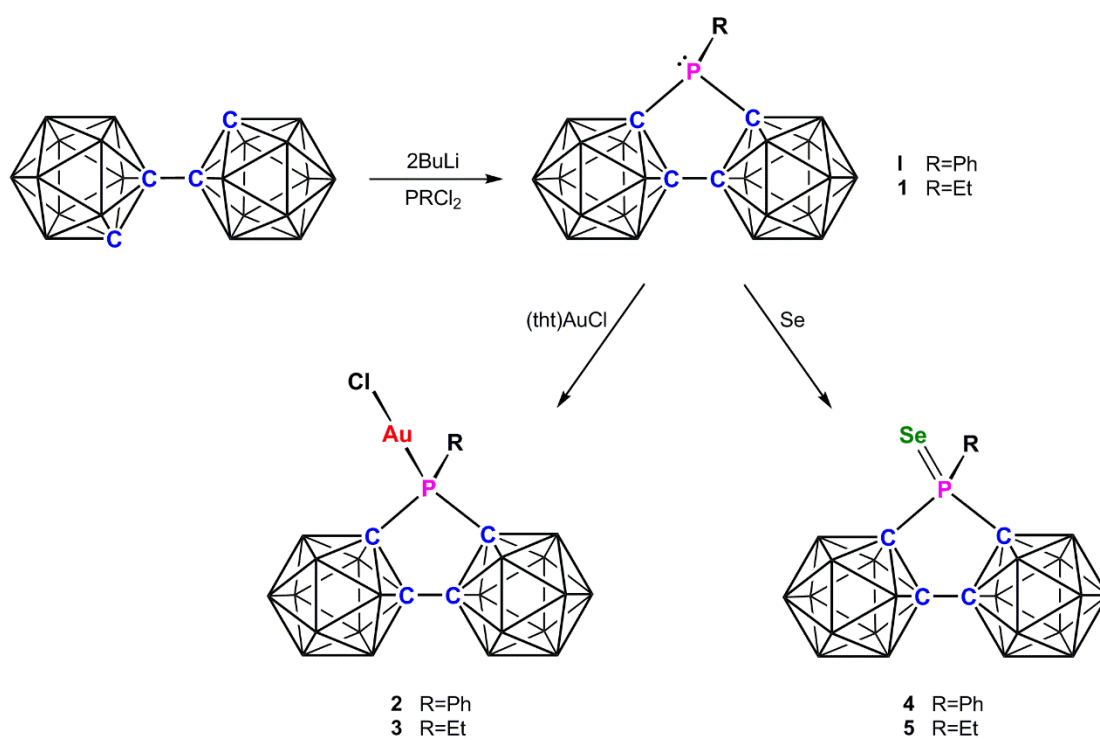


Fig. 10 Perspective view of compound **5** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2. Selected interatomic distances (Å): P1–Se1 2.0801(7), P1–C2 1.879(2), P1–C2' 1.893(2), P1–C11 1.822(2), C1–C1' 1.543(3).



Scheme 1 Generalised reaction scheme for compounds **1** and **1-5**.

Table 1 Tolman cone angles ($\theta/^\circ$) and % V_{bur} for bis(carborane)phosphines **I** and **1** and their complexes with {AuCl}, **2** and **3** respectively.

	θ	% V_{bur}
I	172.5	32.0
1AB	171.6	30.9
1CD	171.6	30.7
2	176.2	33.2
3	176.5	32.0

Table 2 X–P–C11–C12 torsion angles ($^{\circ}$) and key dihydrogen bonding (\AA) in bis(carboranyl)phosphines and related compounds.

(i) Phenyl substituent

compound	X	X–P–C11–C12	dihydrogen bond	distance	dihydrogen bond	distance
I	lp	–29.4(2)	H16 \cdots H6'	2.15(3)	H16 \cdots H3	2.48(2)
2	Au	–28.8(3)	H16 \cdots H6'	2.20(3)	H16 \cdots H3	2.49(3)
4	Se	–40.0(2)	H16 \cdots H6'	2.19(2)	H16 \cdots H3	2.84(2)

(ii) Ethyl substituent

compound	X	X–P–C11–C12	dihydrogen bond	distance	dihydrogen bond	distance
1AB	lp	38.8(4)	H11P \cdots H6B	2.28(5)	H11P \cdots H3A	2.45(5)
1CD	lp	42.5(4)	H11X \cdots H6D	2.29(5)	H11X \cdots H3C	2.39(4)
1_{DFT}	lp	38.4	H11PX \cdots H6'	2.10	H11PX \cdots H3	2.28
3	Au	37.7(3)	H11A \cdots H6'	2.32(3)	H11A \cdots H3	2.52(4)
3_{DFT}	Au	39.8	H11A \cdots H6'	2.17	H11A \cdots H3	2.34
5	Se	48.6(3)	H11A \cdots H6'	2.40(3)	H11A \cdots H3	2.46(2)
5_{DFT}	Se	39.9	H11A \cdots H6'	2.14	H11A \cdots H3	2.29

Table 3 Crystallographic data.

	I	1	2	3 ·1.25CH ₂ Cl ₂	4	5
CCDC	1527028	1527029	1527030	1527031	1527032	1527033
Formula	C ₁₀ H ₂₅ B ₂₀ P	C ₆ H ₂₅ B ₂₀ P	C ₁₀ H ₂₅ AuB ₂₀ ClP	C ₆ H ₂₅ AuB ₂₀ ClP	C ₁₀ H ₂₅ B ₂₀ PSe	C ₆ H ₂₅ B ₂₀ PSe
<i>M</i>	392.47	344.43	624.89	683.00	471.43	423.39
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	<i>P</i> bar1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> bar1
<i>a</i> /Å	7.1139(10)	23.441(2)	17.0588(8)	10.4380(13)	10.3457(12)	7.1663(7)
<i>b</i> /Å	11.4378(14)	7.2690(6)	14.2499(7)	17.711(2)	16.9431(17)	11.0308(15)
<i>c</i> /Å	13.3912(15)	24.083(2)	20.0698(9)	27.475(3)	13.6941(14)	14.573(2)
α /°	81.884(5)	90	90	90	90	111.478(9)
β /°	84.954(5)	108.290(5)	102.497(3)	90	105.612(6)	92.125(9)
γ /°	81.231(6)	90	90	90	90	104.679(6)
<i>U</i> /Å ³	1063.6(2)	3896.2(6)	4763.1(4)	5079.3(10)	2311.9(4)	1026.2(2)
<i>Z</i> , <i>Z'</i>	2, 1	8, 2	8, 1	8, 1	4, 1	2, 1
<i>F</i> (000)/e	400	1408	2368	2596	936	420
<i>D</i> _{calc} /Mg m ⁻³	1.225	1.174	1.743	1.786	1.354	1.370
μ (Mo-K α)/mm ⁻¹	0.127	0.128	6.357	6.224	1.693	1.898
θ _{max} /°	26.46	23.77	32.01	27.24	28.95	30.14
Data measured	15395	44057	58934	33633	43105	40190
Unique data, <i>n</i>	4334	5928	8266	5651	6088	5691
<i>R</i> _{int}	0.0636	0.1415	0.0796	0.0526	0.0740	0.0763
<i>R</i> , w <i>R</i> ₂ (obs. data)	0.0685, 0.1260	0.0795, 0.1841	0.0342, 0.0602	0.0297, 0.0585	0.0365, 0.0767	0.0410, 0.0861
<i>S</i> (all data)	1.135	1.053	1.015	1.020	1.034	1.036
Variables	340	609	358	323	349	315
E _{max} , E _{min} /e Å ⁻³	0.31, -0.35	0.48, -0.41	0.93, -1.81	0.69, -0.65	0.35, -0.42	0.61, -0.58

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